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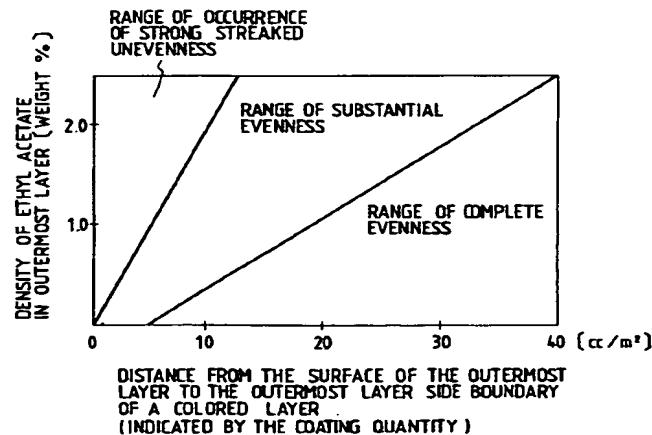
㉒ Coating method.

㉓ A coating method for producing a photographic light-sensitive element without unevenness of coating, even when coating is carried out with at least one coating composition containing a low boiling point solvent as an outermost layer and coating is carried out at a high speed using a multi-layer simultaneous coating method. In accordance with the invention, the following relationship is maintained:

$$C < 0.2L$$

where C (wt%) is the density of a low boiling point solvent in a coating composition forming an outermost one of the coating layers, and L (cc/m<sup>2</sup>) is a quantity of a wet coating per web unit area in a thickness from an outermost layer side boundary of a silver halide containing layer inside said outermost layer to a surface of said outermost layer.

*FIG. 1*



**BACKGROUND OF THE INVENTION**

The present invention relates to a method for applying a liquid solution to a running web for use in producing photographic films, photographic printing paper, etc., (hereinafter referred to collectively as "photographic light-sensitive elements"), and particularly relates to a multi-layer simultaneous coating method.

In producing photographic light-sensitive elements, generally, emulsions of a so-called oil-in-water dispersion type is used. In producing such an emulsion, sometimes a low boiling point solvent such as ethyl acetate, butanol, or the like is used as an auxiliary solvent. When a liquid coating containing such a low boiling point solvent is used to form the outermost layer in a multi-layer simultaneous coating method, it is difficult to obtain a stable and uniform film coating. This is because if such a low boiling point solvent is contained even in small amounts in the outermost layer, the solvent in the liquid surface can easily be evaporated by contacting only a very weak flow of air. The nonuniform distribution of surface tension in the free surface of the coating composition caused thereby produces disorder of the liquid films and hence unevenness of coating.

To prevent such uneven coating from occurring, the following methods have been proposed:

(1) a method whereby the content of an organic solvent contained in the coating composition is made to be not more than 5 wt% (see, for example, Japanese Unexamined Patent Publication No. Hei. 3-92846); and

(2) a method whereby the content of a solvent in the outermost layer is made to be not more than 1 wt%, or a method using an apparatus for weakening the air flow over the coated portion by use of an air shield (see, for example, Japanese Patent Application No. Hei. 1-320640).

However, in the case where the distance from the outermost vapor-liquid surface to the silver halide containing layer is small, or in the case where a large quantity of a low boiling point solvent is contained in the layer next to the innermost layer, it is not sufficient to use only the above-mentioned stabilizing method, even if the content of low boiling point solvent in the outermost layer is not more than 1 wt%. Uneven coating still results because of the uneven surface tension distribution caused by nonuniform evaporation on the liquid surface of the low boiling point solvent. Therefore, in the case where the silver halide containing layer is close to the liquid surface, when any thickness unevenness in coating occurs, even if it is slight, the thickness of the silver halide containing layer will also be nonuniform.

If the distance between the liquid surface and the silver halide containing layer is made long, no unevenness in coating occurs, even if the content of the low boiling point solvent in the outermost layer is about 1 wt%. In the case where a larger quantity of low boiling point solvent is contained in the inner layer next to the outermost layer, on the other hand, the low boiling point solvent contained in the inner layer will diffuse to the outermost layer liquid surface and evaporate to thereby cause unevenness in coating before the liquid film is deposited on the web and gels thereon, even if the content of the low boiling point solvent in the outermost layer is zero.

Such uneven coating can be reduced by appropriately selecting the type and content of the surface-active agent in the outermost layer. This is because such uneven coating is caused by the uneven surface tension distribution produced on the liquid surface. Such surface tension distribution is apt to be produced particularly in the case where the liquid surface is expanded. Therefore, uneven coating can be reduced by appropriately selecting the type and content of the surface-active agent so as to relieve the surface tension when the liquid surface is expanded.

**45 SUMMARY OF THE INVENTION**

It is accordingly an object of the present invention to provide a coating method in which coating can be carried out without producing any unevenness in the applied coating, even if at least one layer of the coating composition includes a low boiling point solvent as the outermost layer thereof and the coating composition is applied at a high speed by the use of a multi-layer simultaneous coating method.

The foregoing and other objects of the present invention are attained by a multi-layer simultaneous coating method for performing coating of a photographic light-sensitive element constituted by at least two layers, characterized in that the following relationship is satisfied:

55  $C < 0.2L$

where  $C$  (wt%) represents the density of a low boiling point solvent in the coating composition for the outermost layer, and  $L$  (cc/m<sup>2</sup>) represents the quantity of wet coating per web unit area within the thickness

from the outermost layer side boundary of a silver halide containing layer inside the outermost layer to the surface of the outermost liquid layer.

Also, the density of a low boiling point solvent in an inner layer next to the outermost layer is preferably not less than 0.5 wt% nor more than 7 wt%.

5 The surface-active agent in the outermost layer may be of a type and be supplied in such a quantity that a difference of surface tension between points of film heights 0 and 6 cm measured by a film breaking method in passing time on the surface is within a range of not more than 5 dyne/cm.

10 For the multi-layer simultaneous coating method to be used in the present invention, known methods may be used. That is, a slide hopper coating method, for example, as disclosed in Japanese Examined Patent Publication No. Sho. 33-8977 or the like may be used. Also, a curtain coating method, for example, as disclosed in Japanese Examined Patent Publication No. Sho. 49-24133 may be used.

15 Examples of the web to be used in the practice of the present invention include paper, plastic films, resin coated paper, synthetic paper, and the like. Examples of the plastic film materials include, for example, polyolefins such as polyethylene, polypropylene, etc.; vinyl polymers such as polyvinyl acetate, polystyrene, etc.; polyamides such as 6, 6-nylon, 6-nylon, etc.; polyesters such as polyethylene terephthalate, 6-naphthalate, etc; polycarbonate; and cellulose acetates such as cellulose triacetate, cellulose diacetate, etc. As for resin used for resin coated paper, polyolefins such as polyethylene, etc., are typically used, but the invention is not so limited. As for paper, polyolefin-laminated paper may be used, and the surface of the paper may be either smooth or embossed.

20 Examples of the coating composition containing a low boiling point solvent include various liquid composites selected according to usage, for example, a coating composition containing water soluble binders such as a silver halide emulsion layer, a primer coating layer, a protective layer, a filter layer, a backing layer, etc., in the case of photographic light-sensitive elements.

25 Examples of the low boiling point solvent to be used in the present invention include, for example, alcohols such as methanol, ethanol, n-propanol, etc.; ketones such as acetone, methylketone, etc.; and esters such as methyl acetate, ethyl acetate, n-buthyl acetate, etc.

30 Examples of the surface-active agent to be used in the present invention include, for example, a nonionic surface-active agent such as glycidol derivatives, fatty-acid esters of multi-valent alcohol, alkyl esters of sugar, etc.; an anionic surface-active agent containing a base such as a carboxyl group, a sulfo group, a phosphoric group, a sulfuric ester group, etc.; and a fluorine-containing surface-active agent. Examples of the above-mentioned anionic surface-active agent include, for example, agents such as those as disclosed in Japanese Unexamined Patent Publication No. Sho. 53-21922 and Japanese Examined Patent Publication No. Sho. 56-1617, and sulfate of high grade alcohol, a high grade alkyl sulfonate, dialkyl sulfo-succinate,  $\alpha$ -sulfonate, and the like. Examples of the fluorine containing surface-active agent include such agents as disclosed, for example, in Japanese Examined Patent Publications Nos. Sho. 47-9303 and Sho. 52-2508, and Japanese Unexamined Patent Publication No. Sho. 60-109548.

35 According to the present invention, the feature that the relationship of  $C < 0.2L$  is satisfied, where  $C$  (wt%) represents the density of a low boiling point solvent in the outermost layer and  $L$  (cc/m<sup>2</sup>) represents the quantity of wet coating per web unit area, results in reducing the unevenness in coating to a level where there is no problem in practical use. However, it is more preferable that the relationship of  $C < 0.08L - 0.4$  be satisfied. On the other hand, if  $C$  and  $L$  are such as to satisfy the relationship of  $C \geq 0.2L$ , extreme unevenness occurs in coating to the extent of causing severe problems in practical use.

40 According to the present invention, that the density of a low boiling point solvent contained in an inner layer next to the outermost layer is made to be not more than 7 wt% reflects the facts that the amount of unevenness in coating becomes a problem in a practical use with a density of not less than 7 wt%, but that there is no problem if the density is not more than 7 wt%. It is more preferable to select the density to be not more than 3 wt%.

45 To reduce the density of the solvent in the coating composition, for example, in the case where the coating composition contains oil-in-water dispersion type emulsions produced by the use of a low boiling point solvent as an auxiliary solvent, there has been employed a desolvent treatment of the emulsion. As for the desolvent treatment of the emulsion, treatments which have been known for stabilizing emulsions, particularly for stabilization in passing time on the surface, may be used, as disclosed, for example, in Japanese Examined Patent Publication No. Sho. 61-56010 and Japanese Unexamined Patent Publications Nos. Sho. 53-112731 and Sho. 53-74031. In this case, generally, the desolvent agent is limited to the extent of 10 wt% of the initial content in an oil-in-water dispersion type emulsion. Further, since the coating composition containing such an emulsion can be diluted with a silver halide emulsion, water soluble binder, water, or the like, the density or the solvent can be reduced.

Increasing the distance between the outermost layer liquid surface and the outermost layer side boundary of the silver halide containing layer can be realized by adding water to the outermost layer or a layer between the outermost layer and the outermost silver halide containing layer. Particularly in the case where the outermost layer contains much low boiling point solvent, the addition of water to the outermost layer may provide effects such that not only can the distance be increased, but also the density of the low boiling point solvent can be reduced.

#### BRIEF DESCRIPTION OF THE DRAWINGS

10 Fig. 1 is a diagram for distinguishing states of unevenness of coating in the relationship between the distance (expressed by the quantity of coating cc/m<sup>2</sup>) from the surface of the outermost layer to the outermost layer side boundary of a colored layer; and  
 Fig. 2 is a diagram illustrating the relationship between film height and surface tension for different types of surface-active agents.  
 15 Fig. 3 shows an outline of an apparatus for measuring surface tension by a film breaking method.

#### DESCRIPTION OF THE PREFERRED EMBODIMENTS

20 The effects of the present invention can be confirmed by the use of colored layers, which can indicate unevenness of coating more clearly than silver halide containing layers.

##### **Comparative Example 1:**

25 Simultaneous coating of two layers was performed with the composition shown in Table 1 using a slide hopper coating apparatus.

Table 1

30	Component	No. 1 colored layer (wt%)	No. 1 outermost layer (wt%)
	Gelatin	8.0%	8.0%
	H <sub>2</sub> O	90.7%	89.6%
35	Ethyl acetate (low boiling point solvent)	0.0%	2.0%
	Anionic surface-active agent dodecyl benzene sodium sulfonate	0.0%	0.05%
	Water soluble dyestuff	1.0%	0.0%
40	Water soluble thickener	0.3%	0.3%
	Viscosity (centipoise)	50	50
	Quantity of coating (cc/m <sup>2</sup> )	60	10.2

45 With the density of ethyl acetate in the outermost layer being 2.0 wt% under the density of a low boiling point solvent C, multi-layer simultaneous coating was performed on a cellulose triacetate film under the conditions that the coating quantity of the colored layer was 60 cc/m<sup>2</sup>, the coating quantity of the outermost layer was 10.2 cc/m<sup>2</sup>, and the coating speed was 100 m/min. As a result, coating unevenness in the form of parallel streaks or streaks slightly shifted parallel to the advancing direction was strongly produced in the 50 coated surface. The relationship between C and L was C = 2  $\div$  2.04 = 0.2L.

##### **Example 1:**

55 Using the same colored layer as in Comparative Example 1, while changing the liquid composition and the coating quantity of the outermost layer as shown in Table 2, two layer simultaneous coating was performed twice with respect to two types of outermost layer in connection with the same colored layer.

Table 2

(wt%)

Component	No. 2 outermost layer	No. 3 outermost layer
Gelatin	6.0%	4.0%
H <sub>2</sub> O	92.2%	94.4%
Ethyl acetate (low boiling point solvent)	1.3%	1.0%
Anionic surface-active agent dodecyl benzene sodium sulfonate	0.05%	0.05%
Water soluble thickener	0.4%	0.5%
Viscosity (centipoise)	50	50
Quantity of coating (cc/m <sup>2</sup> )	19.8	30

With respect to the density C of the low boiling point solvent, the density of ethyl acetate was 1.3 wt% in the second outermost layer and 1.0 wt% in the third outermost layer. The coating quantity was 19.8 cc/m<sup>2</sup> for the second outermost layer and 30 cc/m<sup>2</sup> in the third outermost layer. The evaluation on the result of coating was as follows:

In the second outermost layer, unevenness in coating was hardly seen, and the relationship between C and L was  $C = 1.3 < 3.96$ .

In the third outermost layer, no unevenness at all in coating was observed, and the relationship between C and L was  $C = 1.0 < 6.00$ .

In general, the more the values of C and 0.2L were separated, the better the obtained result in the coating unevenness.

Further, Fig. 1 shows results obtained by detailed investigations into the influence on the production of coating unevenness by the density of a solvent in the outermost layer, and the distance from the outermost layer side boundary of a colored layer further interior than the outermost layer with respect to the liquid surface under the above-mentioned conditions.

#### Example 2:

Setting the coating quantities of the outermost layer and the colored layer to 10.2 cc/m<sup>2</sup> and 60 cc/m<sup>2</sup>, respectively, using the same composition for the outermost layer as in Comparative Example 1, while changing the composition of the colored layer among the three types shown in Table 3, two layer simultaneous coating was performed three times with respect to the three types of colored layers in connection with the same outermost layer.

Table 3

(wt%)

Component	Colored layer			Outermost layer
	No. 2	No. 3	No. 4	No. 4
Gelatin	8.0%	8.0%	8.0%	8.0%
H <sub>2</sub> O	90.7%	83.7%	80.7%	90.6%
Ethyl acetate/methanol (l/l)	0.0%	7.0%	10.0%	1.0%
Anionic surface-active agent dodecyl benzene sodium sulfonate	0.0%	0.0%	0.0%	0.05%
Water soluble dyestuff	1.0%	1.0%	1.0%	0.0%
Water soluble thickener agent	0.3%	0.3%	0.3%	0.3%
Coating quantity (cc/m <sup>2</sup> )	60			10.2

The content of a low boiling point solvent in the colored layer was set to 0 wt%, 7 wt%, and 10 wt%, while the content of the low boiling point solvent in the outermost layer was 1.0 wt%.

As a result, in the second colored layer, streaked unevenness of coating was hardly seen, in the third colored layer, streaked unevenness was present in the coating but to an extent producing no problem in practical use, and in the fourth colored layer, strong streaked unevenness in the coating was produced.

The relationship between C and 0.2L was C = 1 < 2.04 in each case.

It can be understood from the above that good results can be obtained if the content of the low boiling point solvent in the colored layer is not more than 7 wt%, and streaked unevenness is reduced if the content of the low boiling point solvent in an inner layer next to the outermost layer is also made not more than 1 wt%.

### Example 3:

The surface-active agent p-dodecyl benzene sodium sulfonate was replaced by:

- a: polyoxyethylene octyl phenyl ether ethane sodium sulfonate of equivalent mole;
- b: diethyl sulfo sodium succinate of equivalent mole; and
- c: diethyl sulfo sodium succinate of five-fold moles.

The other conditions of the liquid composition were the same as in Comparative Example 1.

When coating was performed under these conditions, for the surface-active agent a, streaked unevenness of the resulting coating was produced, but to an extent that there would be no problem in practical use. For the surface-active agent b, streaked unevenness of the resulting coating was hardly observed, while for the surface-active agent c, no streaked unevenness of the resulting coating was observed at all.

Further, the surface tension in each case was measured by a film breaking method in passing time on the surface. As shown in Fig. 2, the amount of streaked unevenness of coating is reduced if the conditions are set such as to reduce the change of surface tension. Although this result was obtained in the case of using 2 wt% ethyl acetate, almost the same result can be obtained in the range of 0 to 7 wt%. As for C and L, to eliminate problems of streaked unevenness in practical use for various surface-active agents, the following conditions should be maintained:

Comparative Example 1 (p-dodecyl benzene sodium sulfonate):

C < 0.2L

5

a. (polyoxyethylene octyl phenyl ether ethane sodium sulfonate):

C < 0.25L

10

b. (dioctyl sulfo sodium succinate):

C < 0.3L

15 Unevenness of coating can be improved if a surface-active agent having a small change of surface tension in passing time on the surface is used.

The film breaking method used herein is a method for measuring surface tension in passing time on the surface, as disclosed, for example, in detail in Japanese Unexamined Patent Publication No. Hei. 3-20640. The measuring apparatus discussed in Hei. 3-20640 for measuring the surface tension comprises: two-dimensional optical sensor system containing an optical axis perpendicular to the liquid film through a subject portion to measurement of the liquid film; A/D convertor; and calculating circuit to calculate an angle of the subject portion to subject a digital signal from the A/D convertor to approximation relating to a shape of the edge of the liquid film by a multiple dimensional curve. Since the measuring apparatus can calculate the measured value in a moment corresponding to the shape of the edge of the broken liquid film by an image processing, it is able to provide an apparatus realizing a precision measurement of the surface tension and increasing the number of kinds of measured subjects. Namely, the above apparatus realizes to use a formula containing many factors as follow;

$$2\sigma = Q \cdot u \cdot \sin^2 \theta + \rho \cdot S \cdot g \cdot \sin \theta - \rho \cdot S \cdot v^2 / R$$

30

wherein, Q: flow rate in unit width, u: falling velocity,  $\theta$ : inclination of an edge of a liquid,  $\sigma$ : surface tension, S: cross section of a liquid film at the edge of the broken film,  $\rho$ : density of the liquid, v: velocity in the edge of the liquid film, R: radius of curvature of a liquid edge.

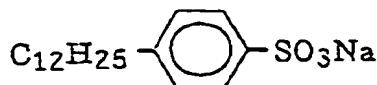
Furthermore, a structure of the apparatus for measuring surface tension to perform the film breaking method is shown in Fig. 3. In Fig. 3, a liquid injected from a slit 2 of a extrusion type injector 1 forms a thin film 4 which is supported by a free fall supporting member 3. The thin film 4 is broken as like an arch 6 by a low-wetting type bar 5 which is inserted into the thin film 4. In the measuring method, an inclination  $\theta$  of an edge of a liquid at a measuring point 7 for the surface tension is subjected to image processing by a two dimensional CCD camera 9 to display of an image thereof on a monitor 10 and to calculation of the surface tension by a calculator 11.

The condition that the difference of surface tension measured at two points of the film heights 0 and 6 cm from the slit 2 of the injector 1 in Fig. 2 is not more than 5 dyne/cm by use of values of surface tension measured by the film breaking method may be used as a standard to select the type and density of a surface-active agent having a small change of surface tension in passing time on the surface.

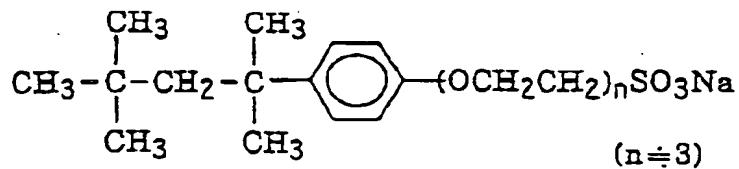
45 Structural formulae of the surface-active agents used in this example are shown in the following formulae 1 to 3.

[Formula 1] : p-dodecyl benzene sodium sulfonate,

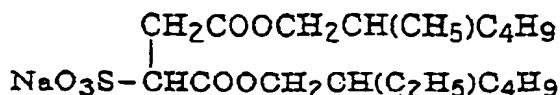
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55 [Formula 2] : polyoxyethylene octyl phenyl ether ethane sodium sulfonate,



10 [Formula 3] : dioctyl sulfo sodium succinate,



20 According to the coating method of the present invention, it is possible to perform coating without producing unevenness of coating, even if the coating is performed at a high speed by use of a multi-layer simultaneous coating method.

25 **Claims**

1. In a multi-layer simultaneous coating method for producing a photographic light-sensitive element comprising at least two layers, the improvement wherein the following relationship is satisfied:

30  $C < 0.2L$

35 where C (wt%) is the density of a low boiling point solvent in a coating composition forming an outermost one of said layers, and L (cc/m<sup>2</sup>) is a quantity of a wet coating per web unit area in a thickness from an outermost layer side boundary of a silver halide containing layer inside said outermost layer to a surface of said outermost layer.

40 2. The coating method of claim 1, wherein a density of a low boiling point solvent in a layer next to said outermost layer is in a range of 0.5 to 7 wt%.

45 3. The coating method of claim 1, wherein a surface-active agent of a type and in a quantity yielding a difference of surface tension between points of film heights 0 and 6 cm, measured by a film breaking method in passing time on the surface, within a range of not more than 5 dyne/cm is used as a surface-active agent in said outermost layer.

50 4. The coating method of claim 1, wherein the following relationship is satisfied:

55  $C < 0.08L - 0.4.$

5. The coating method of claim 1, wherein a density of a low boiling point solvent in a layer next to said outermost layer is not more than 3 wt%.

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FIG. 1

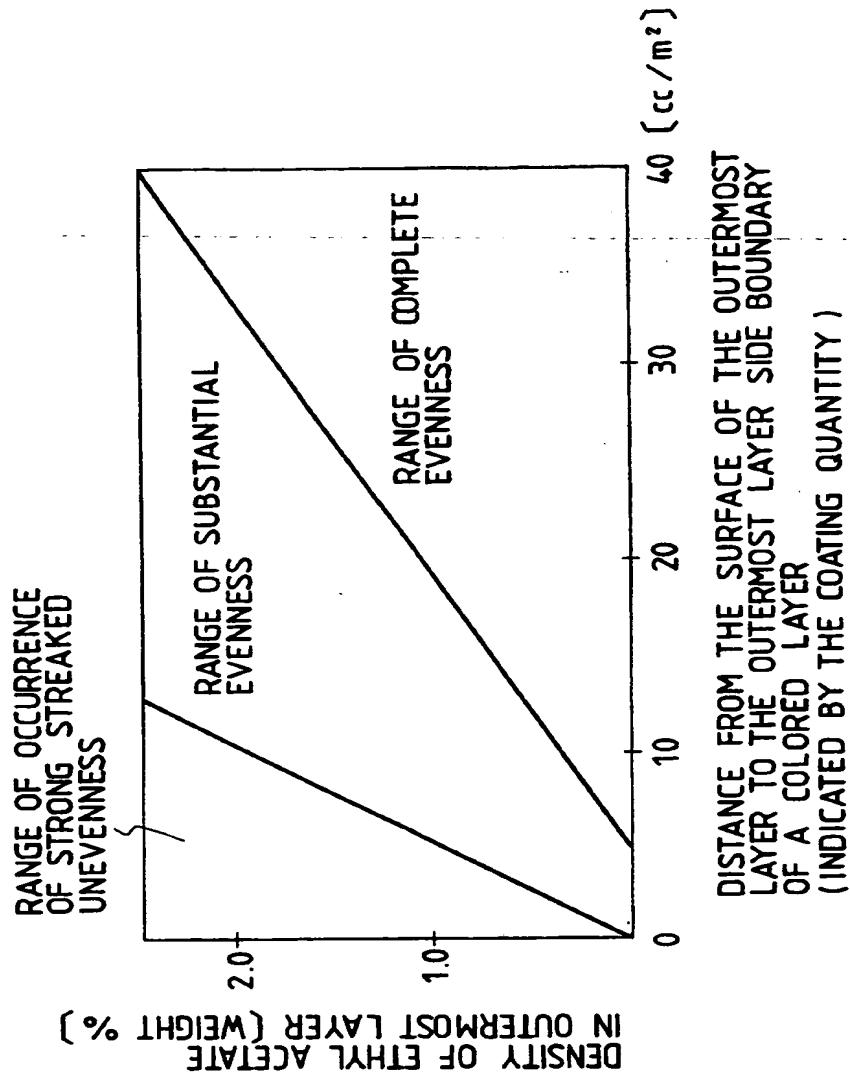


FIG. 2

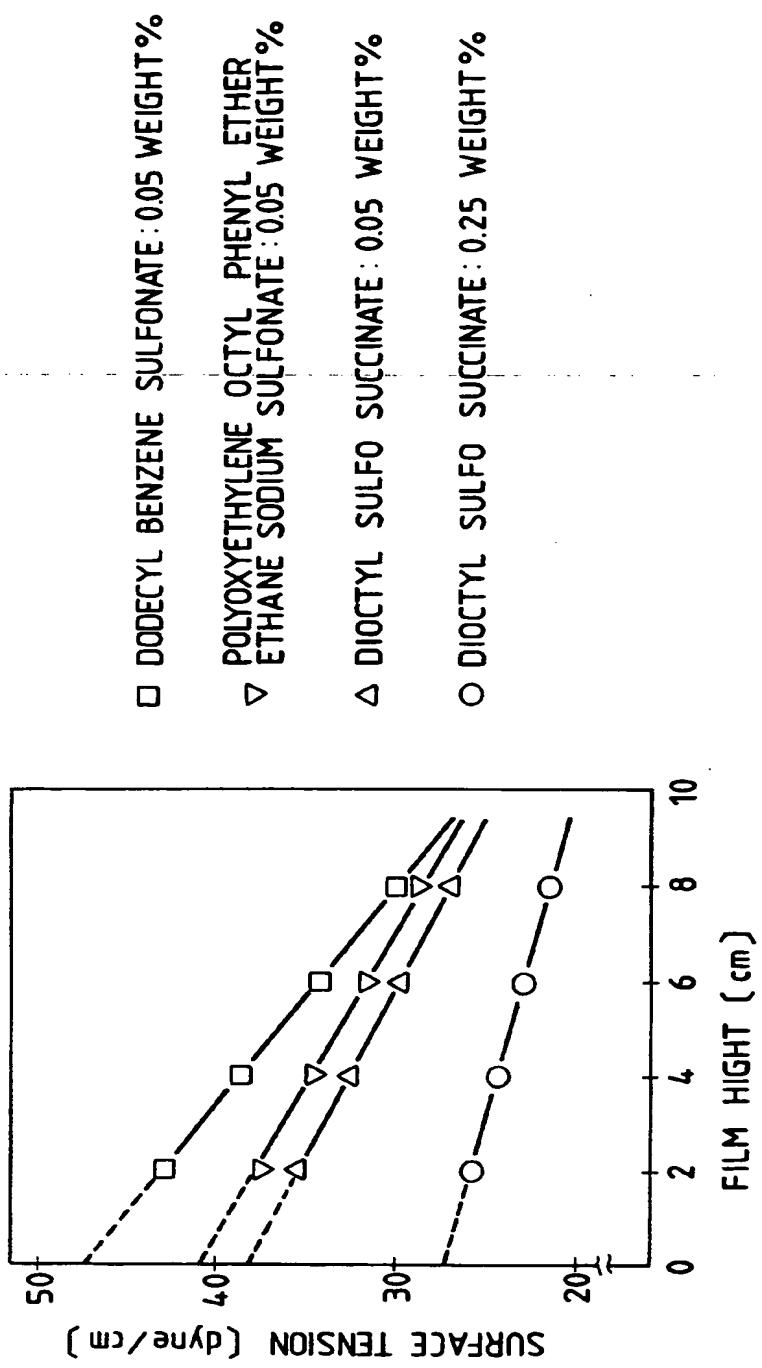
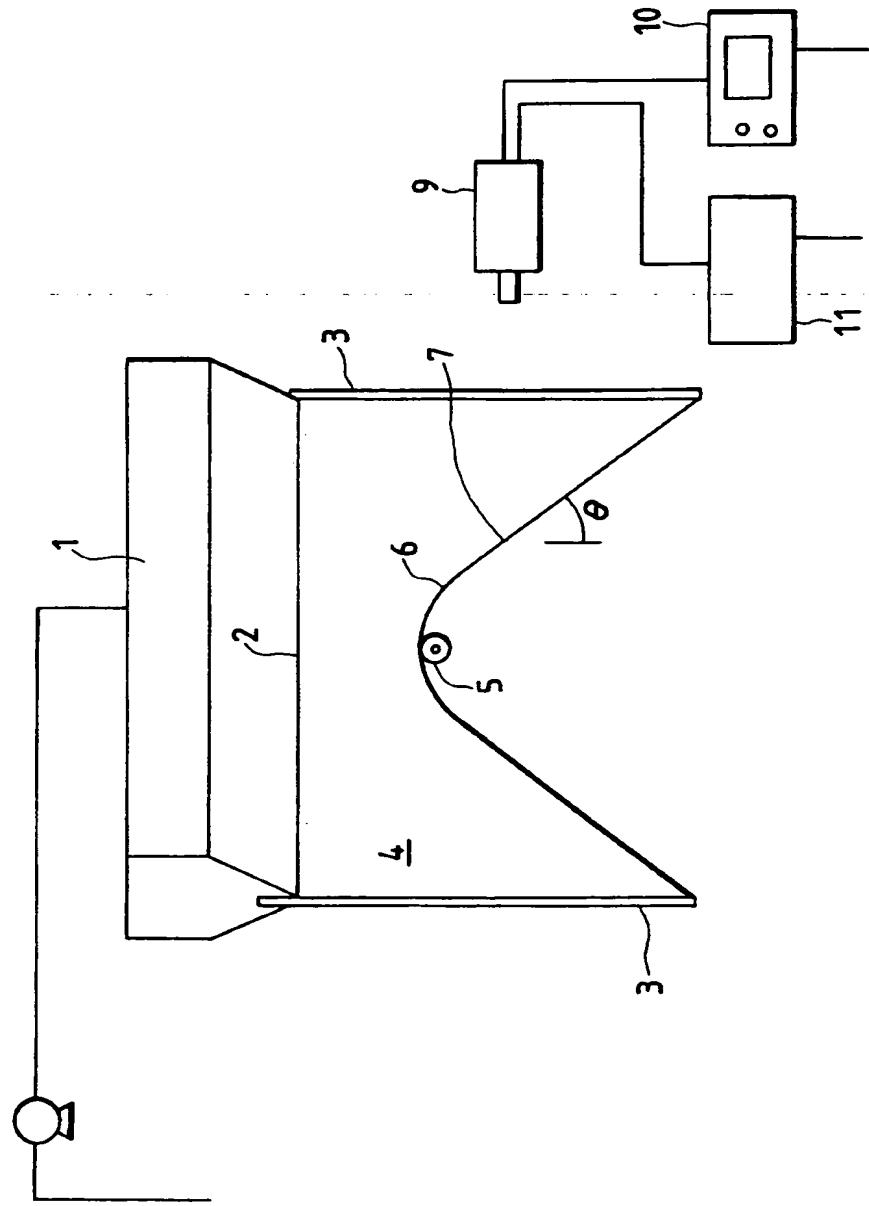


FIG. 3





European Patent  
Office

EUROPEAN SEARCH REPORT

Application Number

EP 92 11 7749

DOCUMENTS CONSIDERED TO BE RELEVANT			CLASSIFICATION OF THE APPLICATION (Int. CL.5)
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	
A	PATENT ABSTRACTS OF JAPAN vol. 14, no. 138 (P-1022) 15 March 1990 & JP-A-20 03 045 ( KONICA CORP ) 8 January 1990 * abstract * ---	1-5	G03C1/74
D,A	PATENT ABSTRACTS OF JAPAN vol. 15, no. 431 (C-881) 5 November 1991 & JP-A-31-81-368 ( FUJI PHOTO FILM CO LTD ) 7 August 1991 * abstract * ---	1-5	
D,A	PATENT ABSTRACTS OF JAPAN vol. 15, no. 274 (P-1226) 11 July 1991 & JP-A-30 92 846 ( KONICA CORP ) 18 April 1991 * abstract * -----	1-5	
			TECHNICAL FIELDS SEARCHED (Int. CL.5)
			G03C
The present search report has been drawn up for all claims			
Place of search	Date of compilation of the search	Examiner	
THE HAGUE	21 JANUARY 1993	BARATHE R.	
CATEGORY OF CITED DOCUMENTS		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons ----- & : member of the same patent family, corresponding document	
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